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## PICOSECOND INTERBAND SATURATION AND INTRABAND RELAXATION OF PHOTOEXCITED CARRIERS IN GERMANIUM

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**Résumé** - Nous présentons de nouveaux faits expérimentaux concernant la saturation interbande du germanium à l'échelle picoseconde. Nous avons utilisé la technique d'excitation-sonde pour une étude systématique de plaquettes de germanium cristallisé d'épaisseur 6  $\mu\text{m}$ , en fonction de la température, de l'énergie de l'impulsion excitatrice et du retard excitation-sonde. Les impulsions sont produites par un laser à verre dopé au Néodyme. Les résultats peuvent être interprétés avec succès en termes de remplissage dynamique de bandes par une distribution de porteurs chauds avec une contribution de l'absorption inter-bandes de valence dans le cas des plus fortes densités ( $\sim 10^{20} \text{ cm}^{-3}$ ). Nous observons que l'accroissement de la transmission de l'échantillon, dépendant de l'intensité, peut dépasser 200 psec sous certaines conditions et que ceci est en accord soit avec un refroidissement lent des porteurs chauds, soit avec une diffusion.

**Abstract** - We report new structure in the picosecond interband saturation of germanium. The excite-probe technique has been employed in an extensive study of a 6 -  $\mu\text{m}$ -thick slice of crystalline germanium as a function of temperature, excite pulse energy, and time delay between the excite and probe pulses from a Nd-glass laser. The results can be interpreted successfully in terms of a dynamic band-filling by a hot carrier distribution with intervalence-band absorption contributing at the highest carrier densities ( $\sim 10^{20} \text{ cm}^{-3}$ ). An intensity-dependent rise in sample transmission is observed that can exceed 200 psec under certain conditions and that is consistent with either a slow cooling of the hot carriers or with diffusion.

Investigations of the nonequilibrium electronic properties of semiconductors on a picosecond time scale are still comparatively rare, and our knowledge of ultrafast transient processes at large carrier densities is limited, even though the rewards from a greater understanding of these processes could be high in terms of ultrafast device applications, laser annealing, and laser damage mechanisms. Since 1974, various optical excite and probe techniques<sup>1-17</sup> have been employed in an extensive study of the picosecond evolution of nonequilibrium high-density photogenerated carrier distributions in germanium. These studies have demonstrated the importance of parametric coupling,<sup>1,3,14</sup> Auger recombination,<sup>4,12</sup> phonon-assisted carrier cooling,<sup>5,11,12,15</sup> diffusion,<sup>2,16</sup> intervalence-band absorption,<sup>12,17</sup> and the dynamic Moss-Burstein shift of the absorption edge (band filling)<sup>3,5,12,15</sup> in determining the picosecond dynamics of the interband absorption of germanium. Nevertheless, serious questions remain regarding the dynamics of the photoexcited excess carriers

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and the precise mechanisms by which they relax, in spite of considerable efforts to theoretically model the possible physical mechanisms involved.<sup>7,10,11,18,19</sup>

Recently, we have employed the excite-probe technique in an extensive study of thin wafers of single-crystal germanium as a function of sample temperature, sample thickness, sample surface preparation, excite pulse energy, and time delay between the excite and probe pulses from a Nd-glass laser with much improved beam characteristics. In the present work, we report new structure in the picosecond interband saturation dynamics of a 6- $\mu\text{m}$ -thick slice of germanium at 100 K. The results can be interpreted successfully in terms of a dynamic band-filling by a hot carrier distribution with intervalence-band absorption (and possibly diffusion) contributing at the highest carrier densities ( $\sim 10^{20} \text{ cm}^{-3}$ ).

The Nd-glass laser produced a train of approximately 40 ultrashort pulses at 1.06  $\mu\text{m}$ . By careful alignment and aperturing, the laser consistently produced a  $\text{TEM}_{00}$  spatial output mode. An electro-optic shutter isolated a single pulse of 7 psec (FWHM) duration, as determined by type I second harmonic autocorrelation techniques. This pulse was divided into two parts by a beam splitter and a variable delay was introduced into one path. The delayed pulse (probe) was attenuated by a factor greater than  $10^3$ . The two pulses, the excite and probe, were recombined after focusing at a small angle on the surface of a slab of crystalline germanium held in a variable-temperature, closed-cycle refrigerator (Fig. 1).

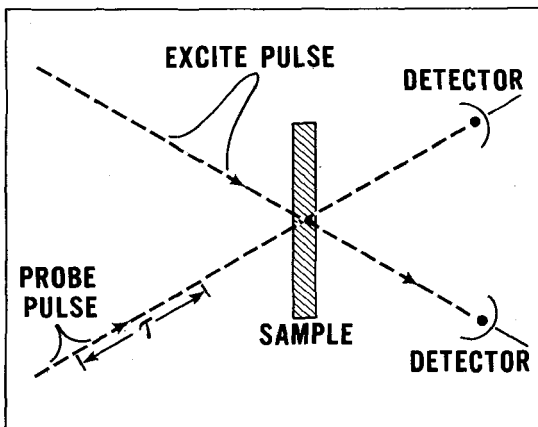
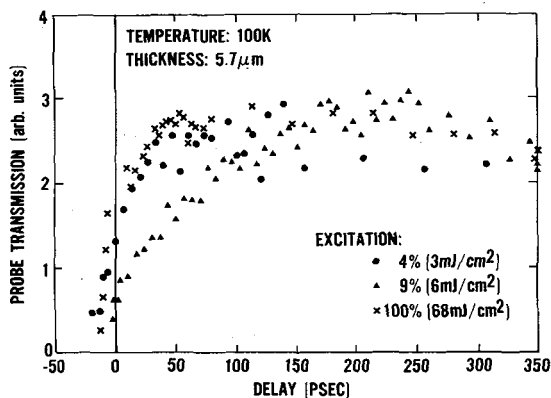


Fig. 1: Schematic of experimental technique.

The single crystal germanium sample, which was mounted on a glass substrate, was polished and syton-etched to a thickness of  $5.7 (\pm 0.5) \mu\text{m}$ , as determined by interferometric techniques. The sample temperature was monitored with a thermocouple attached directly to the crystal. The measured excite beam diameter was  $200 \mu\text{m}$  (FWHM) at the crystal surface; the probe beam was half this size, to ensure that the center of the excited area was monitored. All beam profiles (both before and after focus) were determined by scanning the beam with a small pinhole and were checked with an

optical multichannel analyzer (vidicon detector). The unattenuated peak excite-pulse fluence at the sample was  $100 \text{ mJ/cm}^2$ , corresponding to a peak irradiance of approximately  $13 \text{ GW/cm}^2$ . Experiments were carried out in two separate, but related ways: (1) for specific, fixed excitation energies, the probe pulse transmission was measured as a function of delay after the excite pulse and (2) at fixed delays, the variation of the probe transmission was measured as a function of incident excite-pulse energies.

In experiments of the first type, we found that the time required for the probe transmission to attain its maximum value depends strongly on the excite pulse fluence (intensity). The transmission of the probe pulse was measured as a function of time delay for fixed excitation levels of  $68 \text{ mJ/cm}^2$  ( $\sim 9 \text{ GW/cm}^2$ ),  $21 \text{ mJ/cm}^2$  ( $\sim 3 \text{ GW/cm}^2$ ),  $15 \text{ mJ/cm}^2$  ( $\sim 2 \text{ GW/cm}^2$ ),  $6 \text{ mJ/cm}^2$  ( $\sim 0.8 \text{ GW/cm}^2$ ), and  $3 \text{ mJ/cm}^2$  ( $\sim 0.4 \text{ GW/cm}^2$ ). The results for three of these excitation energies are shown in Fig. 2. Each data point shown is the average of ten laser shots. Error bars have been omitted for clarity. Note that the probe transmission has been plotted in arbitrary units that are normalized to roughly the same peak value for each excitation level to facilitate a direct comparison of the transmission rise. At relatively low excitation fluences of roughly  $3 \text{ mJ/cm}^2$ , the probe transmission rises rapidly and is indistinguishable from the integral of the excite intensity envelope. At  $6 \text{ mJ/cm}^2$ , however, the probe transmission rises much more slowly, taking approximately 200 psec to attain its peak value. At intensities above  $6 \text{ mJ/cm}^2$ , the rise becomes increasingly rapid until at  $68 \text{ mJ/cm}^2$  the rise has the form of an integration effect once again. All excitation levels, including those not shown in Fig. 2 for clarity, smoothly and reproducibly fit this trend.



**Fig. 2:** Excitation dependence of the measured rise in probe transmission with time delay.

In experiments of the second type, the probe transmission has been measured as a function of excitation energy at fixed delays of 0, 15, 50, 150, and 250 psec. The results for four of these delays are shown in Fig. 3. The probe transmission at various fixed delays increases from its Beer's law value, showing a previously

unobserved leveling off at approximately 1% as the excite energy is increased. At larger, fixed delays, this bleaching is more pronounced, and the probe transmission turns over and actually decreases at the highest excite levels. This behavior has been shown to be consistent with the onset of intervalence-band transitions from the split-off valence band to the light and heavy-hole valence bands at high excitation levels.<sup>17</sup> This turnover in the germanium transmission was not resolved in earlier studies, primarily because we could not constrain our previous laser systems to operate in a single transverse Gaussian mode while producing short well-mode-locked pulses. Damage caused by "hot spots" in the multimode beams produced by previous systems prevented our reaching the excitation levels reported here. The largest energies reported in Fig. 3 are within a factor of 2 of the threshold for sample damage. In fact, the multimode nature of the pulses used in previous studies prevented an accurate calibration of the fluence, independent of the technique chosen. The reader should be skeptical of exact fluences quoted for such multimode systems. The excitation energy dependence of the rise in probe transmission reported in Fig. 2 can also be deduced from Fig. 3 by tracing the probe transmission versus time for constant excitation energies. The arrows along the ordinate in Fig. 3 mark the excitation energies chosen for the variable-delay studies described in the previous paragraph.

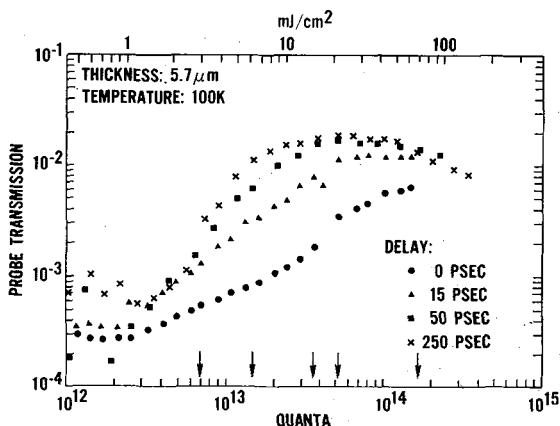


Fig. 3: Measured probe transmission versus excitation fluence for various fixed time delays.

Germanium is an indirect gap semiconductor whose band structure is well known. The relevant features are sketched in Fig. 4. The optically-coupled states for direct absorption between the light and heavy-hole valence bands and the conduction band and for direct absorption between the split-off valence band and the light and heavy-hole valence bands are shown in Fig. 4 for  $1.06 \mu\text{m}$  (1.17 eV) light. The nonparabolicity of the central conduction band valley was considered in determining the coupled energies. Thus, using  $1.06 \mu\text{m}$  light, electrons can initially be excited from the light and heavy-hole valence bands to states in the central conduction band valley that are higher than the minima in the [111] or [100] directions.

Immediately following excitation, these photoexcited carriers will be scattered from their initial states by carrier-carrier and carrier-phonon interactions. Electrons deposited in the central valley can reach the other conduction band valleys by long wavevector phonon scattering. The carriers will, on some time scale, lose energy (cool) within their respective bands by phonon emission. A complete picture of the carrier dynamics must also account for the effects of diffusion and electron-hole recombination.<sup>15,16</sup>

The enhanced transmission of a high intensity excitation pulse (Fig. 3) occurs through the dynamic Moss-Burstein shift of the absorption edge (band filling) caused by the large number of generated carriers.<sup>3,5</sup> The exact magnitude of the absorption change will depend on both the carrier number and carrier temperature. Using known band parameters for germanium, a simple density-of-states calculation shows that at low lattice and carrier temperatures, it requires approximately  $7 \times 10^{18} \text{ cm}^{-3}$  holes to move the quasi-Fermi level to the initial states in the heavy-hole valence band and  $4 \times 10^{19} \text{ cm}^{-3}$  holes for the light-mass band. The equivalent numbers for the conduction band are much higher ( $\sim 5 \times 10^{20} \text{ cm}^{-3}$ ) because of the large number of high effective mass side valleys that must also be filled to the level of the optically-coupled states. Thus, we expect that the principle saturation of the direct interband transitions will be caused by a depletion of valence electrons in the light and heavy-hole bands. More than  $1 \times 10^{20} \text{ cm}^{-3}$  holes are required, at low lattice and carrier temperatures, to lower the quasi-Fermi level in the valence band to a position where the final states are available for direct intervalence-band transitions between the split-off valence band and the heavy and light-hole valence bands. Thus, in principle, at low electron temperatures, the direct interband transitions can be completely saturated before the onset of intervalence-band absorption.

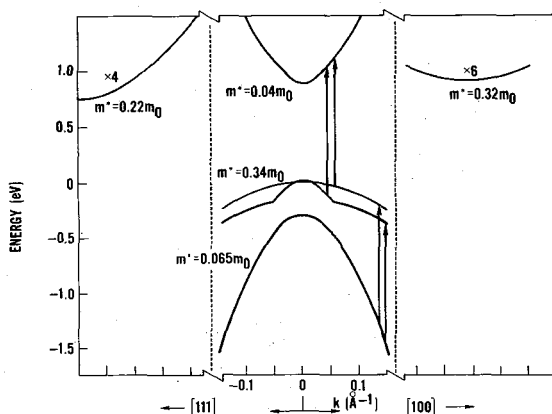


Fig. 4: Sketch of relevant features of the germanium band structure.

The occupancy of the optically-coupled states and, consequently, the transmission are determined not only by the number of carriers but also by their location in

the various bands. The electrons are initially deposited into the conduction band with an excess energy of approximately 0.5 eV, but carrier-carrier scattering ensures rapid thermalization of both the electrons and holes. The resulting Fermi-like distributions for both carrier types can be characterized by a temperature significantly above that of the lattice. A high carrier temperature such as this initially results in a lower transmission since the electrons and holes are located high in their respective bands. As the carrier distribution gives its energy to the lattice by phonon emission (cooling), the transmission should rise.

We have performed a straightforward numerical calculation for the transmission of the excite pulse by integrating over the crystal thickness using the well-known band parameters to determine the initial and final states for valence-to-conduction band and intervalence-band transitions. Gaussian temporal and spatial profiles were assumed for the laser pulse. Comparison of the excite pulse data (identical to 0 delay in Fig. 3) with two extreme cases for the calculation shows that the transmission is too low for the carriers to be at the temperature of the lattice during the passage of the excite pulse, but too high for the carriers to have maintained all of their excess energy above the band gap during generation. A characteristic temperature in the range 600 - 700 K gives good agreement with the measurements. In this case the maximum carrier concentration predicted at the highest excitation energies is approximately  $2 \times 10^{20} \text{ cm}^{-3}$  at the front surface dropping to  $8 \times 10^{19} \text{ cm}^{-3}$  at the back surface of the crystal. That is, the spatial distribution of carriers is within a factor of 3 of being uniform at the highest excitation levels.

Using the predicted carrier concentrations determined by the passage of the excite pulse, we then calculated the expected probe transmission assuming various values for the carrier temperature. Diffusion and recombination effects were neglected during this portion of the study. The results are shown in Fig. 5. Notice that the parametric dependence of the numerically-calculated probe transmission on temperature is identical to the measured dependence of the probe transmission on time (Fig. 3). If this correspondence is correct, it implies a slow cooling of the hot-carrier distribution that can exceed 200 psec. This is much slower than would be expected from a much more complicated, detailed calculation of the cooling rate using the accepted electron-phonon coupling constants.<sup>7,10,15</sup> However, slower cooling mechanisms have recently been suggested involving an optical phonon bottleneck<sup>13</sup> or a screening of the electron-phonon interaction.<sup>19</sup> Notice that our simple parametric analysis avoided the complication of knowing the exact value of the coupling constants or calculating the cooling rate. It only required a calculation of the direct and intervalence-band absorption coefficients as a function of carrier density and carrier temperature.

A similar parametric study involving the effects of Auger recombination in which the carriers were assumed to instantly cool to lattice temperature following

the excite pulse, produced a dependence of the probe transmission on time and excitation level in direct disagreement with experimental results.

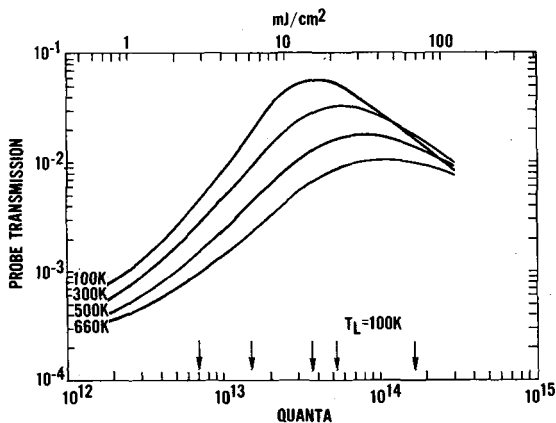


Fig. 5: Theoretically calculated probe transmission versus excitation fluence for various assumed carrier temperatures.

Other mechanisms have been considered at least qualitatively. A model in which the carriers are assumed to have an elevated temperature during the generation processes, are assumed to cool instantly (compared to the optical pulsewidth) following the excite pulse, and then assumed to diffuse away from the sample surface into the bulk has also produced qualitative agreement with the observed tendencies in the data. More quantitative studies are underway. The effects of diffusion can be experimentally identified by repeating the above studies on even thinner samples. For a sample thickness on the order of the inverse of the direct absorption coefficient ( $0.7 \mu\text{m}$ ), the carrier density can be expected to be approximately homogeneous at all excitation levels. Such samples have now been produced and such studies are now underway.

Finally, we note that the measurements described here have been performed for lattice temperatures of 35 K, 100 K, 150 K, 200 K, and 300 K. The time required for the sample to exhibit its peak transmission is found to also depend on temperature. The dependence of the picosecond optical response of germanium on sample temperature and thickness will be reported and analyzed in future publications.

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